PVDF poly(vinylidene fluoride)

PARAMETER	UNIT	VALUE	REFERENCES
GENERAL			
Common name	-	poly(vinylidene fluoride)	
IUPAC name	-	poly(1,1-difluoroethene)	
CAS name	-	ethene, 1,1-difluoro-, homopolymer	
Acronym	-	PVDF	
CAS number	-	24937-79-9	
Formula		$-\!\!\left[CF_2CF_2\right]_n\!\!-$	
HISTORY			
Person to discover	-	Ford, T A; Hanford, W E	Ebnesajjad, S, Fluoroplastics. Vol. 2. Melt Processible Fluoroplastics, William Andrew, 2003.
Date	-	1948 (patent), 1961 (commercialization)	
Details	-	DuPont scientists patented and commercialized PVDF	
SYNTHESIS			
Monomer(s) structure	-	$F_2C{=}CF_2$	
Monomer(s) CAS number(s)	-	75-38-7	
Monomer(s) molecular weight(s)	dalton, g/mol, amu	64.04	
Monomer(s) expected purity(ies)	%	97	
Monomer ratio	-	100%	
Formulation example	-	monomer 100, surfactant 0.1-0.2, initiator 0.05-0.6, paraffin wax 0.03-0.3, chain transfer agent 1.5-6.0	Ebnesajjad, S, Fluoroplastics. Vol. 2. Melt Processible Fluoroplastics, William Andrew, 2003.
Method of synthesis	-	emulsion and suspension polymerization	
Temperature of polymerization	°C	60-90	Ebnesajjad, S, Fluoroplastics. Vol. 2. Melt Processible Fluoroplastics, William Andrew, 2003.
Pressure of polymerization	MPa	2.8-4.8	Ebnesajjad, S, Fluoroplastics. Vol. 2. Melt Processible Fluoroplastics, William Andrew, 2003.
Number average molecular weight, M_n	dalton, g/mol, amu	64,000-380,000	
Mass average molecular weight, M_w	dalton, g/mol, amu	60,000-534,000	
Polydispersity, M_w/M_n	-	1.6-3.2	
Molar volume at 298K	cm^3 mol^{-1}	32.0 (crystalline)	
Van der Waals volume	cm^3 mol^{-1}	25.6 (crystalline)	
Radius of gyration	nm	14.8-26.5	Lutringer, G; Weill, G, Polym, 32, 5, 1896-1908, 1994.
STRUCTURE	-		
Crystallinity	%	32-76; 41-46 (DSC); 33-41 (WAXS)	Ebnesajjad, S, Fluoroplastics. Vol. 2. Melt Processible Fluoroplastics, William Andrew, 2003; Botelho, G; Silva, M M; Goncalves, A M; Sencadas, V; Serrado-Nunes, J; Lanceros-Mendez, S, Polym. Testing, 27, 818-22, 2008.

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PARAMETER	UNIT	VALUE	REFERENCES
Cell type (lattice)	-	monoclinic, orthorhombic	
Cell dimensions	nm	a:b:c=0.496:0.964:0.462 (α); =0.848:0.491:0.256 (β)	Rutleedge, G C; Carbeck, J D; Lacks, D J, Antec, 2163-66, 1996.
Unit cell angles	degree	α:β:γ=90:90:90	
Number of chains per unit cell	-	2	
Crystallite size	nm	3,000-9,000 (spherulite radius)	
Thickness of layer	nm	6.86-6.95 (crystalline); 2.25-3.24	Linares, A; Nogales, A; Sanz, A; Ezquerra, T A; Peruccini, M, Phys. Rev. E, 82, 0.31802, 1-11, 2010.
Spacing between crystallites	nm	2.25-3.24	
Polymorphs	-	α, β, γ, δ	Rietveld, I B; Kobayashi, K; Honjo, T; Ishida, K; Yamada, H; Matsushige, K, J. Mater. Chem., 20, 8272-78, 2010.
Chain conformation	-	TGTG (α); TTTT (β), TTTG (γ); polar version of α (δ)	Li, W; Meng, Q; Zheng, Y; Zhang, Z; Xia, W; Xu, Z, Appl. Phys. Lett., 96, 192905,1-3, 2010.
Lamellae thickness	nm	8-10	Zhao, Z; Chu, J; Chen, X, Radiat. Phys. Chem., 43, 6, 523-26, 1994.
Heat of crystallization	kJ kg^{-1}	35-45	Gradys, A; Sajkiewicz, P; Adamovsky, S; Minakov, A; Schick, C, Thermochim. Acta, 461, 153-57, 2007.
COMMERCIAL POLYMERS			
Some manufacturers	-	Arkema; Solvay	
Trade names	-	Kynar; Hylar, Solef	
PHYSICAL PROPERTIES			
Density at 20°C	g cm^{-3}	1.76-1.83; 1.68 (amorphous); 1.92-1.98 (crystalline)	
Color	-	white	
Refractive index, 20°C	-	1.42-1.49	
Transmittance	%	85-94	
Haze	%	3-13	
Gloss, 60°, Gardner (ASTM D523)	%	25	
Odor		odorless	
Melting temperature, DSC	°C	158-200; 167-169 (main melting peak)	Linares, A; Nogales, A; Sanz, A; Ezquerra, T A; Peruccini, M, Phys. Rev. E, 82, 0.31802, 1-11, 2010.
Crystallization point	°C	92-140	
Degradation temperature	°C	375 (air), 410 (nitrogen)	
Fusion temperature	°C		
Thermal expansion coefficient, 23-80°C	°C^{-1}	0.7-1.8E-4	
Thermal conductivity, 23°C	W m^{-1} K^{-1}	0.17-0.25	Boudenne, A; Ibos, L; Gehin, E; Candau, Y, J. Phys. D: Appl. Phys., 37, 132-39, 2004.
Glass transition temperature	°C	calc.=-67; exp.=-29 to -57	
Specific heat capacity	J K^{-1} kg^{-1}	1,200-1,600 (23-100°C); 960 (melt)	
Heat of fusion	J g^{-1}	50.3-56.1	Mekhilef, N; Hedhli, L; Reynaud, S; Pasquariello, G O, Antec, 1133-38, 2007.
Heat of crystallization	kJ kg^{-1}	19-58	

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PARAMETER	UNIT	VALUE	REFERENCES
Maximum service temperature	^oC	130-150	
Long term service temperature	^oC	150	
Heat deflection temperature at 0.45 MPa	^oC	48-148	
Heat deflection temperature at 1.8 MPa	^oC	36-115	
Vicat temperature VST/A/50	^oC	110-172	
Enthalpy of meltingh	J g^{-1}	104.5	Linares, A; Nogales, A; Sanz, A; Ezquerra, T A; Peruccini, M, Phys. Rev. E, 82, 0.31802, 1-11, 2010.
Acceptor number	-	17.0, 12.1, 10.2	
Interaction radius	-	4.1	
Hildebrand solubility parameter	$MPa^{0.5}$	16.8-18.4	
Surface tension	mN m^{-1}	calc.=33.2; exp.=33.2	Wu, S, J. Adhesion, 5, 39, 1973.
Dielectric constant at 1000 Hz/1 MHz	-	9-10.5/7-9.9	
Dissipation factor at 100 Hz	-	0.03-0.05	
Dissipation factor at 1 MHz	-	0.03-0.05	
Volume resistivity	ohm-m	1.5-2.3E12	
Surface resistivity	ohm	1E13-1E14	
Electric strength K20/P50, d=0.60.8 mm	kV mm^{-1}	63-67	
Arc resistance	MV/m	700	
Coefficient of friction	-	0.14-0.17 (PVDF/steel)	
Diffusion coefficient of water vapor	cm^2 s^{-1} $x10^7$	8.71 (20^{o}C); 5.57 (90^{o}C)	Hansen, C M, Prog. Org. Coat., 42, 167-78, 2001.
Contact angle of water, 20^{o}C	degree	79-93.4; 80 (adv) and 52 (rec)	Lee, S; Park, J-S; Lee, T R, Langmuir, 24, 4817-26, 2008.
Surface free energy	mJ m^{-2}	31.5	
MECHANICAL & RHEOLOGICAL PROPERTIES			
Tensile strength	MPa	14-60	
Tensile modulus	MPa	420-2,200	
Tensile stress at yield	MPa	14-60	
Elongation	%	20-600	
Tensile yield strain	%	3-12	
Flexural strength	MPa	8-78	
Flexural modulus	MPa	200-2,200	
Compressive strength	MPa	55-110	
Izod impact strength, notched, 23^{o}C	J m^{-1}	50-1,000	
Poisson's ratio	-	0.383	
Shore D hardness	-	70-80	
Shrinkage	%	0.2-3	
Brittleness temperature (ASTM D746)	^oC	-53 to 10	
Melt viscosity, shear rate=100 s^{-1}	Pa s	3,000	
Melt index, 230^{o}C/2.16 kg	g/10 min	0.5-45	

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PARAMETER	UNIT	VALUE	REFERENCES
Water absorption, equilibrium in water at 23°C	%	0.02-0.07	
CHEMICAL RESISTANCE			
Acid dilute/concentrated	-	resistant	
Alcohols	-	resistant	
Alkalis	-	resistant (diluted)	
Aliphatic hydrocarbons	-	resistant	
Aromatic hydrocarbons	-	resistant	
Esters	-	non-resistant	
Halogenated hydrocarbons	-	resistant	
Ketones	-	non-resistant	
Good solvent	-	γ-butyrolactone, cyclohexanone, DMA, DMF, DMSO, ethylene, carbonate, NMP	
Non-solvent	-	acetone, alcohols, aliphatic and cycloaliphatic hydrocarbons, chlorinated solvents, MIBK	
FLAMMABILITY			
Autoignition temperature	°C	268	
Limiting oxygen index	% O_2	44-75	
Char at 500°C	%	7	Lyon, R E; Walters, R N, J. Anal. Appl. Pyrolysis, 71, 27-46, 2004.
Heat of combustion	J g^{-1}	14,780	
UL rating	-	V-0	
WEATHER STABILITY			
Excitation wavelengths	nm	490	Martins, P; Serrado Nunes, J; Hungerford, G; Miranda, D; Ferreira, A; Sencadas, V; Lnaceros-Mendez, S, Phys. Lett., A373, 177-180, 2009.
Emission wavelengths	nm	580	
Low earth orbit erosion yield	cm^3 $atom^{-1}$ x 10^{-24}	1.29	Waters, D L; Banks, B A; De Groh, K K; Miller, S K R; Thorson, S D, High Performance Polym., 20, 512-22, 2008.
TOXICITY			
Carcinogenic effect	-	not listed by ACGIH, NIOSH, NTP	
PROCESSING			
Typical processing methods	-	blow molding, extrusion, injection molding, thermoforming	
Processing temperature	°C	195 (melt); 210 (extrusion)	
Processing pressure	MPa	13.8 (injection); 4.14 (back)	
Process time	min	2 (holding)	
Additives used in final products	-	Fillers: barium titanate, calcium carbonate, carbon black, carbon black coated with conductive polymer, copper powder, hafnium powder, lead zirconium titanate, silica, tantalum powder, titanium dioxide, zeolite, zinc sulfide; plasticizers: adipic polyester, dibutyl phthalate, dibutyl sebacate, glyceryl tributylate, tricresyl phosphate; Antistatics: carbon black, glycerol monooleate	

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PARAMETER	UNIT	VALUE	REFERENCES
Applications	-	acid storage tanks, cables, capacitor films, filtration, fuel seals, heating cables for car seats, ignition cable, membranes, reactive liner of warheads, tubing, valves	
BLENDS			
Suitable polymers	-	PA6, PA11, PC, PEEK, PET, PES, PMMA, PS, PVCA	
ANALYSIS			
FTIR (wavenumber-assignment)	cm^{-1}/-	α-phase – 615, 766, 855; CF_2 – 615; CH_2 – 855, 766	Bao, S P; Liang, G D; Tjong, S C, Carbon, 49, 1758-68, 2011.
Raman (wavenumber-assignment)	cm^{-1}/-	γ-phase – 265, 434, 513, 811, 840, 883, 1234; α-phase – 287, 488, 613, 796, 875, 1200, 1429	Ince-Gunduz, B S; Alpern, R; Amare, D; Crawford, J; Dolan, B; Jones, S; Kobylarz, R; Reveley, M; Cebe, P, Polymer, 51, 1485-93, 2010.
NMR (chemical shifts)	ppm	H NMR: OCH_3 – 3.3; OCH_2 – 3.5; $COOCH_2$– – 4.1-4.2; H– – 0.7-2.3	Liu, F; Xu, Y-Y; Zhu, B-K; Zhang, F; Zhu, L-P, J. Membrane Sci., 345, 331-39, 2009.
x-ray diffraction peaks	degree	18.1, 18.8, 20.4	Huang, X; Jiang, P; Kim, C; Liu, F; Yin, Y, Eur. Polym. J., 45, 377-86, 2009.